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(19)(CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Process for Preparing Aspartic Acid Polycondensates with Improved Biological Degradability and Their Use

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Preparation of aspartic acid polycondensates with improved biodegradability and use thereof

5 Abstract

A process for preparing aspartic acid polycondensates with improved biodegradability comprises polycondensing finely divided aspartic acid by thermal polycondensation in solid phase at tem-
10 peratures from 180 to 250°C until not more than 70% by weight of the theoretically possible amount of water which is formed in the course of the polycondensation has been removed from the reaction mixture, and the obtainable polycondensates are useful as detergent and cleaner additives and as scale inhibitor.

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Preparation of aspartic acid polycondensates with improved biode-
gradability and use thereof

5   The present invention relates to a process for preparing aspartic
    acid polycondensates with improved biodegradability by the ther-
    mal polycondensation of aspartic acid and to the use of the poly-
    condensates as additive in detergents and cleaners.

10 Numerous processes are known for preparing aspartic acid polycon-
    densates. One possibility is the thermal polycondensation of
    aspartic acid in the absence of catalysts. Such a process is
    known for example from US—A—5 057 597. In this process, finely
    divided aspartic acid is polycondensed in an agitated powder bed
15 at temperatures from about 180 to 250°C with distillative removal
    of water, the particle size being not more than 150 μm. The
    polymerization takes place in solid phase without melting of the
    aspartic acid crystals. For this reason no sticky phases occur in
    the course of the polycondensation. The reaction products can be
20 carried off for further use without further workup or purifi-
    cation steps.

    US—A—5 221 733 likewise discloses a process for the thermal poly-
    condensation of aspartic acid wherein pulverulent L-aspartic acid
25 is initially heated to a temperature of about 188°C to start off
    the condensation and then the reaction mixture is heated and con-
    densed at a temperature of at least 216°C until at least 80% of
    the aspartic acid has been condensed to form polysuccinimide. The
    polysuccinimide is subsequently hydrolyzed with a base, the prod-
30 uct being a polyaspartic acid salt.

    The above—described processes seek to maximize the conversion of
    the aspartic acid used in the polycondensation. However, they
    have the disadvantage that the polycondensation is accompanied by
35 the formation of by-products which are not readily biodegradable.

    EP—A—0 454 126 discloses using polyaspartic acid in amounts from
    5 to 50% by weight as builder in detergent formulations contain-
    ing from 10 to 40% by weight of at least one surface-active agent
40 and from 5 to 50% by weight of at least one sodium aluminum
    silicate.

    EP—A—0 511 037 discloses detergent formulations comprising for
    example polysuccinimide as at least partially biodegradable
45 builder.

It is an object of the present invention to provide a process for preparing polycondensates of aspartic acid with better biodegradability than those obtained by existing processes.

5 We have found that this object is achieved by a process for preparing aspartic acid polycondensates with improved biodegradability, which comprises polycondensing finely divided aspartic acid by thermal polycondensation in solid phase at temperatures from 180 to 250°C until not more than 70% by weight of the theoreti-
10 cally possible amount of water which is formed in the course of the polycondensation has been removed from the reaction mixture. The aspartic acid polycondensates thus obtainable are used as additive in detergents and cleaners.

15 The process of the present invention involves subjecting a finely divided aspartic acid to thermal polycondensation in solid phase. The aspartic acid can be used in the polycondensation in the form of crystals or as powder. The aspartic acid crystals range in size for example from 0.001 to 5 mm. Aspartic acid powders have
20 for example average particle diameters from 0.05 to 3, preferably from 0.1 to 2, mm. The polycondensation is carried out in customary apparatus, for example in a tumble dryer or in a stirred bed of solids. In the laboratory, the polycondensation is usually carried out in a rotary evaporator. Apparatus suitable for carry-
25 ing out the polycondensation on an industrial scale includes for example paddle dryers, disk dryers, plough share mixers, paddle mixers, extruders, fluidized beds with or without stirring, double cone mixers, rotary tubes, beds of solids with or without stirring, cone mixers, silos, tubular reactors, stirred tanks
30 (especially with crossbeam stirrers), conveyor belts, drum mixers and ball mills.
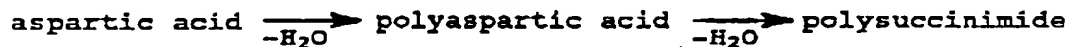
The polycondensation of the aspartic acid according to the present invention is effected thermally, ie. by simply heating finely
35 divided polyaspartic acid to temperatures from 180 to 250°C, preferably 200-240°C. A thermal polycondensation is carried out without the use of catalysts, such as phosphoric acid or hydrochloric acid. Since the aspartic acid crystals do not melt in the course of the thermal polycondensation, no sticky phases occur,
40 so that finely divided polycondensates are obtained. The average diameter and the particle size distribution of the polycondensates obtained substantially correspond to the average diameter and the particle size distribution of the finely divided aspartic acid used as starting material.

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According to the present invention, the polycondensation is carried on only until 70% by weight of the theoretically possible amount of water formed in the course of the polycondensation has been removed from the reaction mixture. The course of the poly-
5 condensation is therefore very easy to monitor by determining the amount of water removed from the reaction mixture. For example, the amount of water distilled out of the reaction mixture can be determined volumetrically or gravimetrically. As soon as 70% by weight, preferably not more than 60% by weight, of the theoreti-
10 cally possible amount of water formed in the course of the poly-condensation has been removed from the reaction mixture, the polycondensation is discontinued by cooling the reaction mixture. To calculate the maximum theoretically possible amount of water which can be eliminated in the course of the polycondensation, it
15 is assumed that the polycondensation of 1 mol (133 g) aspartic acid to polyaspartic acid will on complete conversion release 2 mol (36 g) of water. The weight loss due to the elimination of water during the reaction is thus 27% by weight, based on the aspartic acid used. 70% of the theoretically possible amount of
20 water means that the polycondensation is discontinued when 1.4 mol (25.2 g) of water have been distilled out of the reaction mixture. This corresponds to a weight loss of 18.9%, based on the weight of the aspartic acid used.

25 The polycondensation of aspartic acid can be schematically represented as follows:

aspartic acid $\xrightarrow{-H_2O}$ polyaspartic acid $\xrightarrow{-H_2O}$ polysuccinimide

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Table 1 reveals the nature of the calculation of the amount of water formed in the course of the reaction.

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Table 1
Amount of water distilled out of the polycondensation mixture

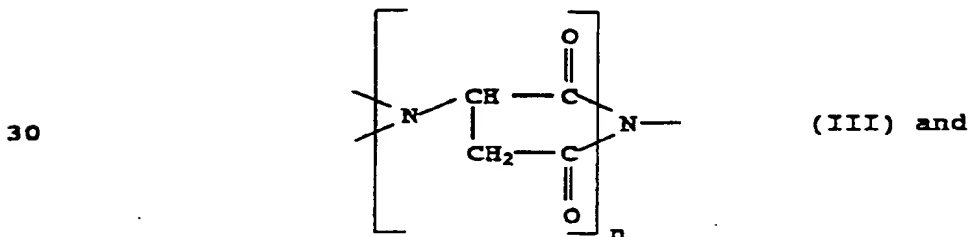| [mol]	% of maximum possible amount	[g]	Based on aspartic acid used [% by weight]
2.0	100	36.0	27.0
1.4	70	25.2	18.9
1.2	60	21.6	16.2
1.0	50	18.0	13.5

The products obtained are aspartic acid polycondensates which contain

a)   alpha- and beta-linked aspartic acid units of the structures

$$-(NH-\underset{\underset{CH_2-COOH}{|}}{CH}-CO)_n- \quad \text{and} \quad -(NH-CH_2-\underset{\underset{COOH}{|}}{CH}-CO)_n-$$

(I)   (II),
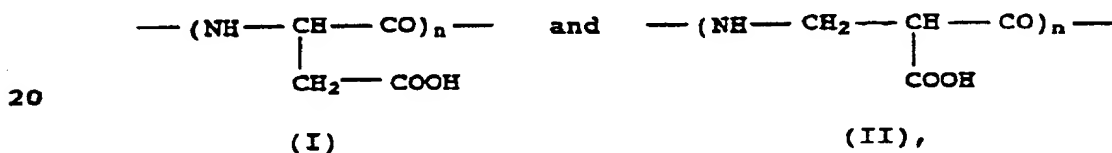
b)   polyaspartimide units of the structure

$$\left[N \underset{\underset{CH_2-\underset{\underset{O}{\parallel}}{C}}{|}}{\overset{\overset{O}{\parallel}}{CH-C}} N- \right]_n$$

(III) and

c)   aspartic acid.

The composition of the polycondensation products depends on the temperature during the polycondensation and on the residence time in the polycondensation zone. The polycondensation can be carried out for example in such a way that no aspartic acid monomer survives into the end product. If, for example, 1 mol of aspartic acid is used and initially 1 mol of water is distilled out of the polycondensation mixture, this will initially result in the formation of 1 mol of polyaspartic acid units, from which 0.4 mol of water is then eliminated to leave 0.4 mol of polysuccinimide units. This means that a polycondensation of 1 mol of aspartic acid where 1.4 mol of water are removed by distillation will give

rise to a product containing 60 mol % of polyaspartic acid units
in the alpha- and beta-form and 40 mol % of polysuccinimide
units.

5   However, the polycondensation can also be carried out in such a
way that, of 1 mol of aspartic acid used, 0.1 mol remains
unchanged in the reaction mixture. On the assumption that 1.4 mol
of water have been removed from the polycondensation of 1 mol of
aspartic acid, the reaction mixture may contain up to 0.4 mol of
10 polyaspartic acid units and up to 0.5 mol of polysuccinimide
units. The polycondensation can also be carried out in such a way
that the use of 1 mol of aspartic acid leaves 0.2 mol of
unchanged aspartic acid behind in the reaction mixture, whereas
the elimination of 1.4 mol of water can lead to the formation of
15 up to 0.2 mol of polyaspartic acid units and up to 0.6 mol of
polysuccinimide units.

Table 2 indicates the compositions of polycondensates on removing
from the reaction mixture 70% - the maximum allowed by the
20 present invention - of the water formed in the course of the
polycondensation.

Table 2
Composition of polycondensates after distillative removal of 70%
25 by weight of the theoretically possible amount of water

Aspartic acid [mol %]	0	10	20	30
Polyaspartic acid [mol %]	60	40	20	0
Polysuccinimide [mol %]	40	50	60	70

The composition of polycondensates after the distillative removal
from the aspartic acid polycondensation mixture of 60 and 50% of
the theoretically possible amount of water is indicated in
35 Tables 3 and 4, respectively.

Table 3

Aspartic acid [mol %]	0	10	20	30
Polyaspartic acid [mol %]	80	60	40	20
Polysuccinimide [mol %]	20	30	40	50

Table 4

Aspartic acid [mol %]	0	10	20	30
Polyaspartic acid [mol %]	100	80	60	40
Polysuccinimide [mol %]	0	10	20	30

The polycondensation is preferably carried out in such a way that in any event the polycondensate contains less than 20 mol % of unchanged aspartic acid. The aspartic acid content of the poly-condensate can range for example from 0 to 19% by weight.

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The aspartic acid condensation products can be analyzed for example using spectroscopic or chromatographic methods. The analytically preparative separation of the reaction mixture into its individual components can be carried out for example by means

10 of an extraction utilizing the differences in the water solu-bility of the individual components.

For instance, the reaction mixture can be extracted first for example with water, in which case the fraction separated off

15 consists essentially of polyaspartic acid or a cocondensate which contains aspartic acid units and succinimide units, the aspartic acid units being present in the cocondensate in an amount of more than 50%. The water-soluble portion isolated from the reaction mixture usually comprises from 20 to 80, preferably from 30 to

20 70, % by weight, based on the aspartic acid used. The water-in-soluble residue is aspartic acid and polysuccinimide. It is treated for further extraction with 1N hydrochloric acid, causing aspartic acid to dissolve by formation of aspartic acid hydro-chloride. The proportion of aspartic acid is usually below 20,

25 preferably below 15, % by weight, based on the amount of aspartic acid used. The residue which is insoluble in water and hydrochlo-ric acid consists predominantly of polysuccinimide and is present in the condensation product in an amount from 5 to 80, preferably from 15 to 70, % by weight. The quantitative determination of the

30 individual fractions is by drying and weighing. The amount of aspartic acid used can be used to calculate the percentage shares of polyaspartic acid and polysuccinimide.

The polycondensation is carried out within the temperature range

35 from 180 to 250°C, preferably within the temperature range from 190 to 250°C. The higher the condensation temperature which is chosen, the shorter is the reaction time. At a polycondensation temperature of 225°C, for example, 50% of the theoretical amount of water formed in the course of the polycondensation can be dis-

40 tilled out of the reaction mixture in the course of a condensa-tion time of about 2.5 h. The reaction mixture then contains 50% of water-soluble polycondensate and 50% of water-insoluble poly-condensate. The K values of the polycondensates of aspartic acid range from 8 to 30, preferably from 10 to 25, determined by the

45 method of H. Fikentscher on 1% strength aqueous sodium salt solu-tions of the polycondensate at pH 7 and 25°C. The molecular

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weights M~ of the polycondensates range from 500 to 7 000, prefer-
ably from 800 to 5 000.

In the Examples which follow, parts are by weight. The K values
5 of the polycondensates were determined by the method of
H. Fikentscher, Cellulose-Chemie 13 (1932), 58-64, 71-74, in
aqueous solution on the sodium salts of the polycondensates at a
concentration of 1% by weight, a pH of 7 and a temperature of
25°C.

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Example 1

A 200 l capacity tumble dryer is charged with 50 kg of L-aspartic
acid (average particle diameter 0.1-2 mm) and heated by means of
15 an external oil cycle to a temperature of 240°C. During the poly-
condensation the reactor is flushed with 100 l of nitrogen/h. As
soon as the temperature of the finely divided aspartic acid has
reached 200°C, the polycondensation starts, as is discernible from
the accumulation of water in the condenser. Once the polycon-
20 densation has started at 200°C it is continued until, after
3 hours, 7.5 l of water have been separated off. This amount of
water of condensation corresponds to a 55% conversion. The poly-
condensate is analyzed extractively and spectroscopically. It is
found to contain 5% of aspartic acid, 50% of water-soluble aspar-
25 tic acid polycondensate and 45% of water-insoluble polysuccini-
mide. The course of the polycondensation is shown in Table 5.

The reaction product is not completely soluble in dimethylforma-
mide. It can be converted with sodium hydroxide solution into the
30 sodium salt of polyaspartic acid. The sodium salt of the con-
densation product, as a 1% strength solution, has a K value of
18.8 at pH 7 and 25°C.

Table 5

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Time [h]	Temperature of oil cycle [°C]	Internal temperature [°C]	Amount of water dis-tilled off [l]	% of theoretic-ally possible amounts of water of condensation
0	20	20	0	0
1	150	110	0	0
2	232	203	dripping	0
3	240	219	3.5	25.9
4	240	228	5.0	37.0

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5	240	228	7.5	55.5
Cooling				

Comparative Example 1

The tumble dryer described in Example 1 is charged with 50 kg of
L-aspartic acid having an average particle diameter of 0.1—2 mm
and heated by means of an external oil cycle to a temperature of
240°C. The reactor is flushed with 100 l of nitrogen/h. As soon as
the temperature of the reaction material has reached 200°C, the
polycondensation starts, as is discernible from the fact that
water collects in the condenser. The amount of water is deter-
mined volumetrically. The polycondensation is continued under the
conditions indicated in Table 6 for 6 h, in the course of which
12.2 l of water separate off. The amount of water distilled out
of the reaction mixture and the theoretically possible amount of
water (100% = 13.3 kg of water) are used to calculate the conver-
sion. It is found to be 92.5%. After the polycondensation has
ended, the reactor is found to contain 37.5 kg of water-insoluble
aspartic acid polycondensate (determined by means of the extrac-
tion method). The reaction product is soluble in dimethylforma-
mide. It can be converted with sodium hydroxide solution into the
sodium salt of polyaspartic acid. The sodium salt of the con-
densation product, as a 1% strength aqueous solution, has a
K value of 26.6 at pH 7 and 25°C.

Table 6

Time [h]	Temperature of oil cycle [°C]	Internal temperature [°C]	Amount of water dis- tilled off [l]	% of theoretic- ally possible amounts of water of condensation
0	20	20	0	0
1	180	105	0	0
2	235	203	dripping	0
3	238	217	2.0	14.8
4	240	227	5.5	40.7
5	240	227	7.0	51.9
6	240	227	9.0	66.7
7	240	228	10.3	76.3
8	240	230	12.5	92.6
Cooling				

Examples 2 to 14

A rotary evaporator is charged in each case with 133 g (1 mol) of aspartic acid (particle diameter 0.1-2 mm) and heated in an oil bath which has the temperature indicated in Table 7 for the time indicated in Table 7.

Table 7

Ex.	Temp. [°C]	Time [h]	% of theoretically possible amount of water of condensation	K value of polycondensate hydrolyzed with NaOH
2	240	1	74	18.0
3	240	0.5	49	12.0
4	240	0.25	40	10.0
5	190	5	9	8.0
6	190	7	14	8.7
7	190	16	31	12.4
8	200	3	11	8.5
9	200	6	27	10.8
10	200	16	39	14.1
11	210	2	17	9.7
12	210	7	34	12.8
13	220	2	22	10.4
14	220	6	35	13.7

Correlation between K value and M_w

K value	M_w
9	1000
10	1400
13	2300
15	2800
26	6500

Ecological tests

Ecological tests were carried out in accordance with the modified Zahn-Wellens test as laid down in the OECD Guidelines for Testing of Chemicals (1981), 302 B. The DOC starting concentration (DOC = dissolved organic carbon) was 200 mg/l.

The course of the DOC decrease is listed in Table 8 for the polycondensates prepared in Example 1 and Comparative Example 1.

5 It is clearly apparent from the DOC decrease that early discontinuation of the polycondensation at 55.5% conversion can be used to improve the ecological properties of the polyaspartic acid. For instance, 48% of the polycondensate are rapidly biodegraded within one day without adaption, whereas it takes 20 days to achieve 40% degradation in the case of the comparative example. 10 After an adaption phase of 20 days, Example 1 gives further degradation up to 90%. In the case of the comparative example, the degradation values only rise to 80%.

Table 8

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Time [d]	Decrease in dissolved organic carbon	
	Example 1	Comparative Example 1
0	0	0
1	48	11
2	50	12
4	52	16
8	52	20
12	51	42
20	53	40
28	74	54
48	90	80

30 Result:

Measures according to the present invention make it possible to achieve a distinct improvement in the degree of degradation of the aspartic acid polycondensates over the first 8 days. In addition, higher final degradation values are achieved at the 35 end.

The polycondensates of Examples 2, 3 and 4 were subjected to a Zahn-Wellens test. By day 20 the dissolved organic carbon had decreased to the values indicated in Table 9.

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Table 9

Example	Decrease in dissolved organic carbon by day 20 [%]
2	44
3	69
4	87
Comparative Example 1	40

Application tests
The polycondensates of aspartic acid prepared by the process of the present invention are suitable for use as water treatment agents. The polycondensates of Example 1 and Comparative Example 1 were tested for calcium ion compatibility by preparing in each case aqueous solutions containing 45 ppm of polycondensate and 1000 ppm of calcium ions and determining the transmissivity of the solutions. Both aqueous solutions were found to have a transmissivity of 99.8%, i.e. neither sample combines with calcium ions to form sparingly water-soluble calcium salts.

The polycondensates of Example 1 and Comparative Example 1 were also tested for dynamic calcium carbonate inhibition at a concentration of 2 ppm of polycondensate:

Calcium carbonate inhibition (2 ppm of polycocondensate concentration)

Two test solutions are prepared. Test solution 1 is water having a hardness of 20° (German) and a magnesium hardness of 10° (German). Test solution 2 is an aqueous solution having a sodium carbonate hardness of 4.7° (German) and a sodium bicarbonate hardness of 12.3° (German).

A 500 ml capacity round-bottom flask equipped with stirrer, reflux condenser and gas inlet tube is charged with 150 ml of test solution 1 and 150 ml of test solution 2 and also 2 ppm of the in-test polymer and heated at 70°C for 1 hour or 2 hours while air is being passed in at a rate of 3 l/h. The flask contents are cooled down and filtered through a fluted filter. The filtrate is titrated complexometrically to determine the calcium content in a conventional manner.

The following calcium carbonate inhibition values were determined:

	CaCO₃ inhibition after	
	1 hour	2 hours
Example 1	45 %	37 %
Comparative Example 1	51 %	47 %

As the results show, both polycondensates inhibit the formation
of calcium carbonate. When used as water treatment agents, for
example for scale inhibition, the polycondensates are usually
used in amounts from 1 to 500, preferably from 2 to 100, ppm.

The polycondensates obtainable by the process of the present
invention are also suitable for use as detergent additive.

The polycondensation products obtainable by the process of the
present invention can be included in detergents and cleaners
either directly or in the form of the alkali metal, alkaline
earth metal or ammonium salts. Preference is given to using the
sodium salts of the polycondensates. They are obtainable by
treating the polycondensates with aqueous bases. Instead of the
sodium salts it is also possible to use ammonium salts, for
example the salts formed by treating polycondensates prepared
according to the present invention with ethanolamine,
diethanolamine or triethanolamine. The polycondensates are
included in phosphate-free or reduced-phosphate detergents (ie.
detergents having a phosphate content of less than 25% by weight,
calculated as trisodium polyphosphate) to enhance the detergency
and as incrustation inhibitor. The amounts of polycondensate
range from 0.1 to 50, preferably from 1 to 30, % by weight, based
on the detergent or cleaner.

Some of the polycondensates prepared by the process of the
present invention were subjected to the CD test and also to a
determination of the clay-detaching power in the presence of
nonionic surfactants (the test methods are indicated for example
in WO-A-94/11486).

The results obtained in the CD test and the effectiveness test
were as follows:

Example	τ [min]	Effectiveness [%]
1	340.2	89.2
2	291.8	81.3

3	367.2	75.4
4	383.8	76.4
Comparative Example 1	328.7	87.7

As the results show, the effectiveness values and the dispersing constants of the polycondensates prepared according to the present invention correspond to those of completely polycondensed aspartic acids.

The test of the clay-detaching power in the presence of nonionic surfactants indicates an effectiveness of 93% for polycondensates as per Example 1 and of 89% for the polycondensates of Comparative Example 1.

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We claim:

1. A process for preparing aspartic acid polycondensates with
    improved biodegradability, which comprises polycondensing
    finely divided aspartic acid by thermal polycondensation in
    solid phase at temperatures from 180 to 250°C until not more
    than 70% by weight of the theoretically possible amount of
    water which is formed in the course of the polycondensation
    has been removed from the reaction mixture.

2. A process as claimed in claim 1 wherein the proportion of the
    theoretically possible amount of water formed in the course
    of the polycondensation which is removed from the reaction
    mixture is not more than 60% by weight.

3. The use of the aspartic acid polycondensates obtainable as
    claimed in claim 1 or 2 as additive in detergents and clean-
    ers and as scale inhibitor.

4. A use as claimed in claim 3 wherefor the aspartic acid poly-
    condensates are used in the form of the alkali metal, alka-
    line earth metal or ammonium salts.